Copper(I) and Silver(I) Halide and Pseudohalide Complexes in Water and Dimethylsulfoxide

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II. Ahrland, S., Tagesson, B. and Tuhtar, D.
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1. INTRODUCTION

1.1 Background

During the last century a lot of effort has been devoted to elucidate the nature of metal complexes formed in solution. Essentially this work has concerned with aqueous solutions. Among the first systems to be investigated was copper(I) chloride, bromide and iodide.[1] Other systems e.g. silver halides have been reinvestigated several times with various techniques since those early days of coordination chemistry.[2] The same interest and effort has not been spent on the coordination chemistry of copper(I), however. In the present series of investigations, the thermodynamics of the formation of copper(I) halide and thiocyanate complexes in water and in the aprotic solvent dimethylsulfoxide (DMSO) has been studied. An investigation on the silver halide systems in water has also been performed.

1.2 Systematization of equlibrium data

A useful systematization of the huge amount of stability constants obtained for various complexes[2] was introduced by Ahrland et al.[3] In a purely empirical division, based on the stabilities of complexes in aqueous solution they divided the acceptors into two groups (a) and (b). The typical (a) acceptor forms the most stable complex with the lightest donor atom of each group, while a typical class (b) acceptor forms the most stable complex with one of the heavier members of the groups. Thus the two groups are characterized by the following affinity sequences of donor atoms.

class (a)	class (b)
F >> Cl > Br > I	F << Cl < Br < I
O >> S > Se > Te	O << S < Se ~ Te
N >> P > As > Sb	N << P > As > Sb

Pearsson[4] has afterwards introduced the designation hard for class (a) and soft for class (b) acceptors. The adjectives hard and soft refer to the polarizability of the acceptors. However, a high polarizability is not enough to constitute a typical soft acceptor, rather it is a combination of high polarizability and many d-electrons.[5,6] The terms hard and soft have also been applied to the ligands preferred by each group.[7]

1.3 Complex formation of hard and soft acceptors and donors

The stabilities of complexes, β_j, are governed by the changes in free energy, $\Delta G^{\circ}_{\beta j}$, enthalpy, $\Delta H^{\circ}_{\beta j}$, and entropy, $\Delta S^{\circ}_{\beta j}$, according to the formula

$$-RT \ln \beta_j = \Delta G^{\circ}_{\beta j} = \Delta H^{\circ}_{\beta j} - T\Delta S^{\circ}_{\beta j} \qquad (1)$$

A large gain of free energy, i.e. the formation of a strong complex thus means that either $\Delta H^{\circ}_{\beta j}$ is strongly negative and/or $\Delta S^{\circ}_{\beta j}$ is strongly positive.

The fact that acceptors and donors giving strong complexes can be divided into two groups strongly suggests that the nature of bonds between acceptors and donors of the two groups is different. Hard-hard interactions are mainly electrostatic while soft-soft interactions are markedly covalent, involving a true exchange of electrons between the donor and acceptor.[8]

Complex formation is, however, a more complicated process than the mere formation of new bonds. All species involved are solvated to various degrees and as a complex is formed these solvate bonds have to be broken. In water the hard acceptors and donors are generally strongly solvated due to the protic and polar nature of the solvent. Thus complex formation means liberation of a lot of water molecules and consequently large gains of entropy, which generally determine the strength of the complexes. The energy gained in the formation of the acceptor-donor bond is often more than counterbalanced by the energy of desolvation of the involved species which result in endothermic reactions.[8,9,10]

Soft acceptors and donors are on the other hand only weakly solvated in aqueous solution, and as a matter of fact the entropy change on their complex formation is often negative or, if positive, contributes only little to the stability of the complexes.[8,9,10] The formation of soft-soft complexes is therefore mainly due to the favourable enthalpy term resulting from the formation of the covalent bond.

Complex formation is evidently very dependent on the solvation of the involved species, which in turn depends on the solvent used. Moreover, specific solvation might occur, e.g. hydrogen bonding to hard ligands in protic solvents.[11] In order to study the effects of solvation the same reactions should be studied in solvents of very different properties and the changes in enthalpy and entropy should be determined.

1.4 Selection of complex systems and solvents

As pointed out previously an acceptor has to possess both a high polarizability and many d-electrons in order to display a typical (b)-

character. Copper(I) is in fact the only oxidation state of a first row transition metal that fulfils these criteria. Its solution chemistry should therefore be of a special interest, and especially its coordination chemistry with the halides, ranging from the mildly soft chloride to the very soft iodide. Rather few investigations have been performed on copper(I) in aqueous solution, however, on account of the disproportionation of Cu^+ and the slight solubility of the neutral complexes CuL. Moreover, the published data show a confusing picture (cf. I). To start with, the aim of these investigations was to study the complex formation between copper(I) and the heavy halides in aqueous solution. The ambidentate thiocyanate ion has also been included in the investigation.

The measurements have also been extended to the chloride and bromide complexes of silver(I), an acceptor closely related to copper(I), in order to see the changes caused by an extra electron shell.

In order to study the effects of solvation, a solvent of properties very different from those of water should be used. The aprotic dimethylsulfoxide (DMSO) has been choosen for this purpose. As no hydrogen bonding is possible in DMSO, large differences in the stabilities of halide complexes are expected between this solvent and water where hydrogen bonding is very strong. In DMSO complexes of the strongly hydrogen bonding Cl^- should be more stable relative to complexes of the weakly hydrogen bonding I^-.

In recent years, DMSO has often been used for investigation of metal complex formation in solution, on account of its many favourable properties. The solubility of electrolytes in DMSO is quite high, partly due to efficient solvatization of dissolved species, and partly to the high

dielectricity constant which prevents electrostatic interaction from becoming predominent. The convenient liquid range, between 18.5 °C and 189.0 °C, is very advantageous. The solvent is also easy to purify by vacuum destillation. It has to be handled with care, however, due to its hygroscopic nature and the fact that it penetrates skin, rubber and many plastics. A compilation of the properties of DMSO has been given in a review by Reynolds.[12]

DMSO is a very good solvent for measurements on copper(I) halide systems for two reasons. At first the monovalent state of copper is much more stable in DMSO than in water, where the extensive disproportionation very much restricts the investigation. Thus the disproportionation constants for the reaction $2\ Cu^{+} \rightleftarrows Cu^{2+} + Cu$ is in DMSO[13] $K_D \simeq 2\ M^{-1}$ as against $\simeq 10^{6}\ M^{-1}$ in aqueous solution.[14] Secondly the rather high solubility[13,15] of the neutral complexes CuL makes a determination of the first constants and the enthalpies of their formation feasible.

2. EXPERIMENTAL TECHNIQUES

2.1 Emf and solubility measurements

The stability constants of copper(I) bromide, iodide and thiocyanate in aqueous solution have been determined potentiometrically. A copper amalgam electrode was used and found to work well. To calculate the concentration of Cu^{+}, it is necessary to know the standard potential of the $Cu^{2+}/Cu(Hg)$ couple and also the constant[14] of the disproportionation equlibrium $2\ Cu^{+} \rightleftarrows Cu^{2+} + Cu(Hg)$.

In order to reach the limits of solubility of CuL, potentiometric mea-

surements were performed where the copper(I) halide or thiocyanate solutions were diluted with a solution of the pure ionic medium. In these measurements eventually the neutral complexes CuL, L = Br^-, I^- or SCN^-, precipitated. The emfs were measured when equlibrium was established and samples were also withdrawn for determination of the solubilities. From the emfs the solubility products were calculated. By means of the solubility data an independent check of the results from potentiometry was possible. Both copper amalgam and copper(I) halide solutions are very sensitive to oxidation and air had to be carefully excluded during the measurements.

2.2 Calorimetric measurements

Due to the slight solubility of the neutral complexes ML, the possibilities to perform calorimetric measurements are severely restricted both for copper(I) and silver(I) halide systems in aqueous solution. In the case of copper(I), the disproportionation of Cu^+ taking place in the absence of stabilizing ligand causes another serious limitation.

Two types of calorimeters have been used to determine the enthalpy changes viz. a titration calorimeter and a reaction solution calorimeter. The titration calorimeter is of the type described by Grenthe et al.[16] In aqueous solutions, it has been used for measurements on the silver chloride and bromide systems and also on the copper(I) chloride system. In the case of the silver systems a silver solution was added to a ligand solution, while for the copper(I) chloride a concentrated chloride solution containing copper(I) was added to a dilute chloride solution (cf. II). The titration calorimeter has also been used for the measurements on the copper(I) halide systems in DMSO. In this solvent measurements can be performed by titrating a ligand solution into a metal

solution. The same technique has been used for copper(II) bromide. These measurements behaved quite normally at low bromide concentrations, but at higher ones other reactions than the complex formation took place. As will be further discussed below copper(II) was reduced by the gold of the calorimeter vessel. This reduction is brought about by the large affinities of both copper(I) and gold(I) for bromide ions.

The reaction solution calorimeter is similar to that described by Sunner and Wadsö.[17] The stirring has been improved, however, in order to bring about the dissolution of the solids used here in a sufficiently short time. The enthalpy for the formation of $AgBr_4^{3-}$ was determined by measuring the heat evolved when small amounts of Ag_2O were dissolved in acid bromide and in acid perchlorate solutions. It was also obtained from the heat of solution of AgBr in a bromide solution. The enthalpies of dissolving copper(I) oxide in acid halide solutions have also been obtained by reaction solution calorimetry. From these measurements, the enthalpies for the following substitution reactions have been calculated:

$$CuCl_3^{2-} + 3\ Br^- \rightarrow CuBr_3^{2-} + 3\ Cl^- \qquad (2)$$

$$CuBr_3^{2-} + 3\ I^- \rightarrow CuI_3^{2-} + 3\ Br^- \qquad (3)$$

2.3 Kinetic measurements

During the calorimetric measurements on copper(II) bromide in DMSO, it was found that gold was oxidized by copper(II) at high bromide concentrations. Further experiments showed that analogous reactions took place in the presence of chloride, iodide or thiocyanate, i.e. any ligand strongly stabilizing copper(I) and gold(I). The rates of these interesting oxidations have been measured spectrofotometrically. These

measurements have also been extended to the oxidation of silver and copper by copper(II) solutions of various halide or thiocyanate concentrations. Metal foils were immersed in the copper(II) ligand solutions. The solutions were stirred at constant speed, and the rate of the oxidation taking place was followed by spectrofotometric analysis of withdrawn samples.

2.4 Conditions of the experiments

The measurements in aqueous solution have been carried out in a medium of ionic strength I = 5 M, with sodium perchlorate as supplementary electrolyte. For the calorimetric measurements in DMSO a medium of ionic strength I = 1 M has been used, with ammonium perchlorate as additional electrolyte. No supplementary electrolyte has been added in the measurements of the rates of reduction of copper(II) solutions by metal foils. All measurements have been preformed at 25 ^{o}C.

3. CALCULATIONS

3.1 Calculation of stability constants and solubility products from emf and solubility measurements

The stability constants were calculated from the potentiometric measurements by means of the graphical methods outlined by Fronaeus[18] and Ahrland et al.[19] The results were checked with the least-squares program "EMK", cf.,[20] which allows the calculation of constants of dinuclear complexes as well. The solubility products have been calculated from the emf of cells containing solutions in equlibrium with solid CuL. From the solubilities determined for these solutions the stability constants have been gained by means of the established methods.[50]

3.2 Calculation of enthalpy changes and stability constants from calorimetric measurements

The enthalpy changes have been calculated from titration calorimetry by means of the least-squares program "Kalori".[21] For the copper(I) chloride system the program "Letagrop Kalle" [22] has also been used as a check. Consistent results were obtained by the two methods.

For well-conditioned systems it is possible to obtain stability constants as well as enthalpy changes from calorimetric measurements. The conditions for such simultaneous determinations have been thoroughly discussed by Christensen et al.[23] They conclude that the equlibrium constants have to be small enough ($0 < \log K < 4$) and that the corresponding enthalpy changes have to be sufficiently large. Since the "Kalori" program allows a simultaneous determination of stability constants and enthalpy changes the measurements on copper(I) halide complex formation in DMSO have been performed without a previous determination of the stability constants for the medium used. These systems are not well suited for a determination of stability constants from calorimetry, however, and a separate investigation of the stabilities is thus necessary.

4. RESULTS

4.1 Aqueous solution

The solubility products, K_s, and the overall stability constants, β_j, of the mononuclear complexes of the aqueous copper(I) and silver(I) halide and thiocyanate systems are collected in Table 1. The values of copper(I) bromide, iodide and thiocyanate obtained from potentiometric and solubility measurements in this investigation are discussed in detail in paper I.

Table 1

Mononuclear overall stability constants for the aqueous copper(I) and silver(I) halide and thiocyanate systems. All constants refer to 25 °C and $NaClO_4$ as neutral salt.

L	log β_j				pK_s	I/M	Ref.
j =	1	2	3	4			
		Copper(I)					
Cl^-		6.06	5.94		7.38	5	14, I
Br^-		6.28	7.45		8.89	5	I
I^-		~8.7	10.43	9.40	12.72	5	I
SCN^-			11.60	12.03	14.77	5	I
		Silver(I)					
Cl^-	3.08	5.40	6.15	5.30	10.10	5	24
Br^-	4.22	7.22	9.10	9.21	12.62	5	25
I^-		10.35	13.20	13.92	16.35	4	26, 27
SCN^-	4.59	8.29	10.06	11.26	12.11	4	28

Polynuclear complexes are indicated in the copper(I) iodide and thiocyanate systems, as has previously been found for copper(I) chloride and also for the corresponding silver systems. For the iodide and thiocyanate systems, the introduction of $Cu_2L_6^{4-}$ brings about a much better fit than if only mononuclear complexes are postulated. The amount of copper present as polynuclear complexes never exceeds 20 % of the total in the concentration range used here, however, so the polynuclear complex formation is not very extensive.

The equlibrium concentrations of Cu^+ and L^- in saturated solutions of

CuL, and hence the solubility products, were obtained from those potentiometric measurements where the solubilities of the neutral complexes CuL were exceeded. The total copper(I) concentrations of these saturated solutions were also measured. These solubility determinations, in combination with the solubility products found, allow an independent determination of the mononuclear stability constants as the amount of polynuclear complexes was insignificant in these solutions. The results agree well with those of the potentiometric investigation.

Table 2

Thermodynamics of the aqueous silver chloride and bromide systems at 25 °C and I = 5 M ($NaClO_4$). ΔG^o and ΔH^o in kJ mol^{-1}, ΔS^o in J mol^{-1} K^{-1}.

	Complex formation			Precipitation	
Ligand	Cl^-	Br^-		Cl^-	Br^-
$-\Delta G^o_{\beta 3}$	35.1±0.2	51.8	$-\Delta G^o_{pr}$	56.8±0.2	72.3±0.2
$-\Delta G^o_{\beta 4}$	30.6±0.7	52.6			
$-\Delta H^o_{\beta 3}$	39±5	55±5	$-\Delta H^o_{pr}$	62.7±0.9	80.0±0.5
$-\Delta H^o_{\beta 4}$	62±9	79.6±1.1			
$-\Delta S^o_{\beta 3}$	14±16	9±18	$-\Delta S^o_{pr}$	20±3	26±2
$-\Delta S^o_{\beta 4}$	105±29	91±14			

The titration calorimetry on the silver(I) chloride and bromide systems yielded the enthalpy changes, $\Delta H^o_{\beta j}$, for the overall formation of the third and fourth silver(I) halide complexes and also the enthalpy changes, ΔH^o_{pr}, for the precipitation of silver halides. The changes in free energy, $\Delta G^o_{\beta j}$ and ΔG^o_{pr}, are calculated from the stability constants and the

solubility products, quoted in Table 1. Combination of these quantities yields the entropy changes $\Delta S^{o}_{\beta j}$ and ΔS^{o}_{pr}. These thermodynamic functions are collected in Table 2. Some of the results obtained from titration calorimetry have been checked by reaction solution calorimetry. The results agree fairly well, cf. II.

Enthalpy changes for the formation of copper(I) halide complexes in aqueous solution are difficult to measure, the most serious obstacle being the strong tendency of copper(I) to disproportionate. The only stepwise enthalpy change that has been possible to obtain is $\Delta H^{o}_{3}(Cl^{-}) =$ $= -19.9 \pm 0.7$ kJ mol^{-1}. The enthalpies for ligand substitution in CuL_3^{2-} according to eqs. (2) and (3) have been obtained from the heats of dissolution of copper(I) oxide in acid halide solutions. The changes in free energy for the same reactions are calculated from the overall stability constants of CuL_3^{2-} ($L = Cl^{-}$, Br^{-} and I^{-}), given in Table 1. The changes in entropy are calculated from eq. (1). These thermodynamic functions are collected in Table 3.

Table 3

Thermodynamics for ligand substitution in the third copper(I) halide complex, at 25 °C and I = 5 M ($NaClO_4$). The values refer to the following reactions:

$$CuCl_3^{2-} + 3\ Br^{-} \rightarrow CuBr_3^{2-} + 3\ Cl^{-} \qquad (2)$$

$$CuBr_3^{2-} + 3\ I^{-} \rightarrow CuI_3^{2-} + 3\ Br^{-} \qquad (3)$$

ΔG^{o} and ΔH^{o} in kJ mol^{-1}, ΔS^{o} in J mol^{-1} K^{-1}.

	(2)	(3)
ΔG^{o}	-8.61±0.13	-17.03±0.12
ΔH^{o}	-12±1	-38±3
ΔS^{o}	-11±3	-69±10

4.2 DMSO solution

4.2.1 Thermodynamic measurements of complex formation

The thermodynamic functions determined calorimetrically for copper(I) halide systems and for copper(II) bromide in DMSO are collected in Table 4. The stability constants are subject to very large errors and so are consequently also the changes of free energy, and of entropy. The constants found are, however, of much the same order of magnitude as those determined in 0.1 M ionic medium[13] (cf. III). The changes in free energies and entropies given in Table 4 are therefore certainly not far off the mark. No measurements have been performed on the copper(I) thiocyanate system as the solubility of the neutral complex CuSCN was found to be only ≃ 2 mM which is a little too low for precise calorimetric measurements.

Table 4

Thermodynamics of the copper(I) halide and the copper(II) bromide systems in DMSO at 25 °C and I = 1 M (NH_4ClO_4). ΔG^o and ΔH^o in kJ mol^{-1}, ΔS^o in J mol^{-1} K^{-1}.

	Copper(I)			Copper(II)
	Cl^-	Br^-	I^-	Br^-
ΔG_1^o	-32	-21.5	-28	-8.9
ΔG_2^o	-27	-17	-19	-6.0
ΔH_1^o	-6.7	-8.6	-12.2	8.2
ΔH_2^o	-7.4	1.3	2.6	6.5
ΔS_1^o	84	43	54	57
ΔS_2^o	66	62	73	42

The copper(II) bromide system was investigated in order to apply a correction for the amount of copper(II) present in the measurements on copper(I) bromide. The copper(II) complexes were so weak, however, that no such correction was necessary. The thermodynamic functions given in Table 4 are calculated from the measurements at low bromide concentration as the reduction of copper(II) by the gold of the calorimeter vessel prevented measurements at high bromide concentration. This oxidation reaction, as well as a number of related ones, have been further studied in a separate investigation.

4.2.2 Kinetic measurements of the oxidation of gold, silver and copper by copper(II).

The reactions between copper(II) halide solutions and metallic copper, silver and gold have been studied in a spectrofotometric investigation. It was found that all three metals were oxidized by copper(II) at sufficiently high halide concentrations. The rate of the oxidation was found to depend upon the halide concentration and that chloride and bromide was about equally efficient to bring about the oxidation. Iodide and thiocyanate are oxidized by copper(II) under the formation of copper(I) iodide or thiocyanate complexes and presumeably triiodide and trithiocyanate ions. Even these solutions were able to oxidize gold, however, and consequently also silver and copper. In all measurements, the starting concentration of copper(II) has been 0.25 mM. Both for silver and gold a certain halide concentration was necessary if the oxidation should be noticeable, while no halide was necessary for the oxidation of copper. The oxidation of silver was rapid already at $[Cl^-] = [Br^-] \simeq 0.25$ mM, while for gold a concentration of $\simeq$ 10 mM was necessary (cf. IV).

5. DISCUSSION

5.1 Introduction

The nature of the species involved in complex formation decides the nature of the coordinate bond. The hard ligands that are preferentially coordinated to hard acceptors are held by essentially electrostatic bonds, while the soft ligands preferred by soft acceptors are held by bonds which are markedly covalent.[5,29] This is obvious from the fact that typically hard acceptors are characterized by a high charge density, i.e. a high ratio of charge to radius. Soft acceptors are, on the other hand, characterized by a combination of many d-electrons and a high polarizability,[5,6] while their charge density is generally low.

For all reactions taking place in solution, the solvation of the species involved is moreover of paramount importance. To bring about a dissolution of ionic compounds, a strong solvation is indeed necessary in order to overcome the lattice free energy.[30] Consequently the solvation energy is considerable for all soluble electrolytes and the bonds between ions and solvate molecules have to be rather strong. Complex formation means that solvate molecules coordinated to the acceptors are substituted by ligands. Evidently as the ligands are solvated as well, complex formation also means a substitution of solvate molecules coordinated to the ligands. Obviously both the nature of the solvent and of the dissolved species are very important for the strength of the solvation. The solvation is a very complex phenomenon, however, since it depends on several kinds of intermolecular forces such as ordinary Coulomb interactions, hydrogen bonding, covalent interactions

and London forces.[30] The situation is further complicated by the fact that the same forces also may act between the solvate molecules which counteracts the solvation.

The properties connected with the dipole character and the structural order of a solvent are of great importance for its solvating ability. A high dipole moment enhances the solvation of hard metal ions as their solvation is generally an ion-dipole interaction. However, the energy needed to tear the solvent molecules out of the bulk solvent depends on the strength of the bonds between the solvent molecules. The structural order of the solvent is also determined from these forces. Hydrogen bonding is the strongest interaction between the solvent molecules,[31] and consequently water has a high structural order.[32,33] Due to the very strong hydrogen bonding in water and the rather modest dipole moment, hard metal ions are consequently expected to be less solvated in water than in a strongly polar aprotic solvent e.g. DMSO. For the solvation of soft metal ions, the donor ability i.e. the softness of the solvent is of utmost importance. In DMSO the oxygen atom is softer than in water and consequently also the soft metal ions are more solvated in DMSO than in water. This is also shown by the exothermic enthalpies of transfer from water to DMSO which is characteristic for both hard and soft metal ions.[30] For soft metal ions even more drastic changes might occur in a solvent possessing a donor atom such as N or S. Such a solvation is of a marked covalent character and consequently very selective for soft acceptors. Thus the free energy of transfer of Li^+ (hard) and Ag^+ (soft) from N,N-dimethylformamide to N,N-dimethylthioformamide are as different as +64 kJ g-ion^{-1} and -87 kJ g-ion^{-1} respectively.[34] Such an interaction might be expected between the S atom in DMSO and the soft

copper(I) and silver ions. Silver is, however, most likely coordinated through oxygen[35] and the same is in all probability the case for the harder copper(I). The same is also true for the very soft mercury(II).[36] The coordinating properties of sulfur in DMSO are evidently very weak. This is partly due to a steric factor caused by the configuration of the DMSO molecule. The main cause is probably the high electronegativity of oxygen, however, which decreases the electron density of sulfur and consequently its donor properties. Simultaneously, the donor properties of oxygen might increase. To extremely soft acceptors, however, sulfur is indeed coordinated. This has been shown for e.g. palladium(II).[37,38] This work also nicely shows the contribution from the steric factor.

Anions have generally a lower charge density than cations. As a rule they are therefore more weakly solvated. The solvation of anions is by no means negligible, however, and they are at least as strongly solvated as metal ions of the same charge density.[30] The halide ions are selectively solvated due to their different hydrogen bonding ability. Thus the halides able to form strong hydrogen bonds are bound to hydrogen in protic solvents e.g. water, while of course no such bonds are formed in the aprotic solvent DMSO.[11] This is nicely illustrated by the heat of transfer of halide ions from water to DMSO, which is 19, 4 and -13 kJ mol^{-1} for Cl^-, Br^- and I^- respectively.[30] Only iodide is more strongly solvated in DMSO, while hydrogen bonding makes the bromide and especially the chloride more strongly solvated in water.

The solubilities of the neutral complexes also depend upon the balance between solvation and lattice free energies. The solvation of such species is generally stronger in the less well-ordered DMSO than in

water. As a consequence the neutral copper(I) halide complexes, CuL, which are quite insoluble in water, are easily soluble in DMSO, and so is also the pseudohalide complex CuSCN. A striking increase of solubility due to a stronger solvation also occurs for HgI_2.[39] Also the complexes AgL ($L^- = Cl^-$, Br^-, I^-, SCN^-) are much more soluble in DMSO than in water, though their solubility even in DMSO is not very high.[40] The relative increase of the solubility is nevertheless of the same order of magnitude as for the copper(I) systems.[30]

Differences in solvation also causes the stabilization of different oxidation states in various solvents. The hydrated Cu^+ disproportionates almost completely in water, while the DMSO solvate of Cu^+ is rather stable (cf. p. 9). The stabilization of copper(I) is even more marked in acetonitrile, also an aprotic solvent but solvating via nitrogen which means that special affinities come into play.[41] Very drastic increases are also encountered for gold(I)[42] and mercury(I)[43] in DMSO relative to water. For metal ions with different oxidation states those of lower charge seems to be more stable in DMSO than in water. A plausible explanation is that acceptors of low charge, i.e. the softer ones, are well solvated in DMSO due to the relatively soft character of oxygen in DMSO, while in water a high charge is necessary in order to tear away the solvent molecules from the three dimensional network structure built up by hydrogen bonding.

As pointed out previously (cf. p. 7), typical hard-hard interactions in water are often entropy controlled, while typical soft-soft interactions are in general enthalpy controlled.[8,9,10] Moreover, the term not controlling the course of the reaction quite often acts to same extent

in the opposite direction. Evidently the changes in the thermodynamic functions on complex formation depend very much both upon the solvation of the species involved and upon the structural order of the solvent. These two factors are obviously very different for water and DMSO. Consequently the thermodynamic functions are expected to be very different in the two solvents. Especially the rule that soft-soft interactions are enthalpy controlled has to be modified for reactions in DMSO. In this solvent, the entropy term is often more important for the stability of the complexes. This is partly due to the stronger solvation of soft species in DMSO, but partly also to the larger freedom gained in the more unordered DMSO by the released solvate molecules on desolvation.

5.2 General conclusions for aqueous solution

5.2.1 The halides

The stabilities of copper(I) halide complexes quoted in Table 1, reveal a (b)-sequence i.e. increasing stability in the order $Cl^- < Br^- < I^-$. For silver a more marked (b)-sequence is found as is to be expected from the softer character of this ion, due to its position in a higher period. Moreover, the third and fourth complexes are formed more readily in the silver than in the copper(I) systems. Of course a (b)-sequence is to be expected from the soft nature of the two acceptors.

The present soft-soft interactions are expected to be exothermic in aqueous solution. As far as they have been possible to determine this is certainly also the case. Thus, for silver(I) chloride and bromide, the formation of the third and fourth complexes has been found to be

strongly exothermic. Also as expected, the coordination of the softer bromide ions is for both steps more exothermic than the coordination of the chloride ion. For copper(I) enthalpy values in aqueous solution are difficult to determine and therefore very scarce. No values for the overall complex formation have been obtained, in spite of strenuous attempts. The enthalpies for the substitution of chloride and bromide in CuL_3^{2-} with bromide and iodide, respectively, are strongly exothermic, Table 3. As for silver(I), the complex formation is evidently more exothermic the softer the ligand. The increasing stability of copper(I) halide complexes in the sequence $Cl^- < Br^- < I^-$ depends, as expected upon an increasingly favourable enthalpy term.

A slight loss of entropy is found in the overall formation of the third silver(I) chloride and bromide complexes, while the entropy loss of the fourth step is very large, Table 2. Within the limits of error, the entropy changes are the same for the two systems. The values of $\Delta S^o_{\beta 3}$ follow the rule that the entropy change is of minor importance for soft-soft interactions in aqueous solution, while the entropy loss for the formation of the fourth complex is unexpectedly large. A similar loss in entropy is also found for the fourth step of the copper(I) cyanide system, ($\Delta S^o_4 = -128 \pm 9$ JK^{-1} mol^{-1}.[44] Mercury(II), also a soft acceptor of configuration d^{10}, shows quite a different pattern, with $\Delta S^o_4(Br^-) = -34$ JK^{-1} mol^{-1} and $\Delta S^o_4(Cl^-) = +5$ JK^{-1} mol^{-1}.[45] The entropy loss is thus much larger at the formation of CuL_4^{3-} and AgL_4^{3-} than at the formation of HgL_4^{2-}. The cause is most probably that the smaller and more highly charged copper(I) and silver(I) complexes are more strongly solvated than the mercury(II) complex.

For copper(I), large entropy losses occur when Cl^- is substituted Br^-

and especially when Br^- is substituted by I^- in the complexes CuL_3^{2-} These losses are caused by the stronger solvation of the harder halide ion which is liberated in the reaction. Consequently the increasing stability of the complexes in the sequence $CuCl_3^{2-} < CuBr_3^{2-} < CuI_3^{2-}$ is due exclusively to the increasingly favourable enthalpy term, while the entropy term is acting in the other direction.

5.2.2 Thiocyanate complexes

The thiocyanate ion coordinates either through the softer sulfur or through the harder nitrogen donor atom. The soft acceptors silver(I) and copper(I) are certainly both coordinated through the sulfur atom.[46] The affinity of thiocyanate for the two acceptors is rather remarkable, however. For copper(I) thiocyanate, the complexes are more stable and the solubility product of CuL smaller than for copper(I) iodide while silver thiocyanate has characteristics fairly similar to those of silver bromide, Table 1. The sulfur donor atom has evidently a relatively much stronger affinity to copper(I) than to silver(I). The copper(I) thiocyanate complexes are even absolutely stronger than the corresponding silver ones. The entropy changes which are presumeably < 0, due to the low hydration and the loss of rotational freedom for the thiocyanate ion, ought to be quite similar for the two systems. Consequently more energy is gained when thiocyanate is coordinated to copper(I) than when it is coordinated to silver(I). This is rather remarkable as generally the coordination of soft ligands to acceptors of a certain group becomes more exothermic, the higher the period of the acceptor. This is a consequence of the fact, that acceptors of a certain electron configuration, in this case d^{10}, become more prone to form covalent bonds as the number of their electron shells increases. In this respect, however,

the coordination of thiocyanate to copper(I) and silver(I) constitutes a striking exception.

In this connexion it should also be pointed out that the value of β_2 is larger for the copper(I) chloride system than for the corresponding silver system which of course means that at least one of the first two complexes is stronger for copper(I) than for silver(I).

5.2.3 Precipitation reactions in the silver systems

For both silver chloride and silver bromide the precipitation is found to be highly exothermic and more so for silver bromide. The entropies decrease on precipitation, which of course is to be expected as the solid phases are more well-ordered than the solutions. More entropy is lost at the precipitation of the bromide than at the precipitation of the chloride. The obvious explanation is the decreasing solvation of the halide ions in the sequence $Cl^- > Br^- > I^-$ (cf. p. 21).

5.3 General conclusions for DMSO solution

Large changes are expected in the stabilities of halide complexes in DMSO relative to water due to the different hydrogen bonding ability of the halides. Thus increases in the stabilities of chloride complexes relative to the iodide ones are foreseen. Consequently the (b)-affinity sequences characteristic of the soft acceptors copper(I) and silver(I) in water are expected to become much less marked in DMSO, or even turn into (a)-sequences. The values ΔG_j^o for the formation of the copper(I) halide complexes quoted in Table 4 definitely show that the (b)-sequence in water is much levelled in DMSO. In the latter solvent, a hybride sequence $Cl^- > Br^- < I^-$ might even exist. It must be borne in mind, however, that

the values of ΔG^{o} and ΔS^{o} quoted in Table 4 are to be considered no more than rough approximations (cf. p. 17). For the silver(I) halide complexes, the chloride and also the bromide ones are considerably more stable in DMSO than in water which results in an almost levelled (b)-sequence in DMSO.[47]

Except for the silver(I) chloride system where a third complex has been claimed,[48] no higher halide or thiocyanate complexes than the second ones are known for silver(I) or copper(I) in DMSO. This is in marked contrast to the conditions in aqueous solution where the higher complexes are fairly important. The matter certainly merits further investigation.

The formation of the first copper(I) halide complex is more exothermic the heavier the halide, Table 4. This is as expected for soft-soft interactions where stronger covalent bonds are formed the softer the ligand. For the second step, however, the enthalpy changes are very different from those encountered in the first step. Thus for chloride, the reaction is still rather exothermic, while it is slightly endothermic for bromide and more so for iodide. The difference between chloride and bromide is moreover unexpectedly large in comparison with that between bromide and iodide. The most probable reason is that a larger desolvation of CuL takes place in the bromide and iodide systems. This would of course be reflected in exceptionally high values of ΔS_2^{o} for these systems. In fact they also seem to be higher than ΔS_1^{o} which is not the case in the chloride system.

The enthalpy changes are on the whole small. Yet the complexes are quite strong due to the large gains of entropy on their formation. This fact certainly partly depends upon the strong solvation of Cu^{+} and CuL,

which also causes both the marked stability of Cu^+ and the large solubility of CuL. Very important is also, however, that the entropy gains are considerably increased by the low order of the solvent molecules in DMSO.

5.4 Copper(II) as oxidizing agent in DMSO

The fact that gold is oxidized by solutions of copper(II) halides in DMSO illustrates very strikingly some of the problems encountered in a novel solvent. The knowledge of chemical behaviour in solution, based mainly on the conditions in water, are no longer valid. Very often reactions that are not possible to foresee take place in the new solvent.

Although both copper and silver are oxidized by copper(II) already in aqueous solution at high halide concentrations,[49] DMSO solutions of copper(II) halides are certainly much more strongly oxidizing. The reason is obviously the very pronounced stabilization of copper(I) in DMSO (cf. p. 22). The oxidation of gold is further strongly promoted by the marked stabilization of gold(I) in DMSO.[42] Like silver(I) and copper(I), gold(I) is evidently very preferentially solvated by DMSO. This means on one hand that the oxidation potential of the Au(I)/Au couple is much lower in DMSO than in water which makes gold much less noble in contact with the former solvent. On the other hand, no further oxidation to gold(III) takes place in DMSO. In this solvent, the oxidation potential of the Au(III)/Au(I) couple is in fact so high that DMSO is oxidized before gold(I).[42] That disproportionation of gold(I), which takes place in aqueous solutions except in the presence of extremely stabilizing ligands such as CN^-, therefore does not occur in DMSO.

The stabilization of gold(I) and copper(I) relative to gold(0) and copper(II) brought about in DMSO by the strong solvation of the monovalent oxidation states is nevertheless not sufficient to make the oxidation of gold possible. To achive this a further stabilization by complex formation is necessary. To this end, only fairly low concentrations of halide ions are needed, however.

The less noble silver is oxidized, though very slowly, by copper(II) in DMSO even in the absence of halide. Addition of halide promotes the reaction tremendously, however. In the case of copper, the reaction is fairly fast even when no halide is present though it becomes markedly faster when halides are added.

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REFERENCES

1. Bodländer, G. and Storbeck, O., Z. anorg. Chem. 31 (1902) 1, 458.
2. Sillen, L.G. and Martell, A.E., Stability Constants of Metal-Ion Complexes, Chemical Society, London 1964 and 1971 (Special Publications No 17 and 25).
3. Ahrland, S., Chatt, J. and Davies, N.R., Chem. Rev. 12 (1958) 265.
4. Pearsson, R.G., J. Amer. Chem. Soc. 85 (1963) 3533.
5. Ahrland, S., Struct. Bond. 1 (1966) 207.
6. Jørgensen, C.K., Ibid. 1 (1966) 234.
7. Pearsson, R.G., J. Chem. Educ. 45 (1968) 581, 643.
8. Schwarzenbach, G., Pure. Appl. Chem. 24 (1970) 307.
9. Ahrland, S., Struct. Bond. 5 (1968) 118.
10. Ahrland, S., Struct. Bond. 15 (1973) 167.
11. Björk, O., Metal Halide and Pseudohalide Complexes in Dimethylsulfoxide Solution. Diss. Lund 1975, p. 16.
12. Reynolds, W.R., Prog. Inorg. Chem. 12 (1970) 1.
13. Foll, A., Le Démézet, M. and Courtot-Coupez, J., J. Electroanal. Chem. 35 (1972) 41.
14. Ahrland, S. and Rawsthorne, J., Acta Chem. Scand. 24 (1970) 157.
15. Suarez, T.E., Iwamato, R.T. and Kleinberg, J., Inorg. Chim. Acta, 7 (1973) 292.
16. Grenthe, I., Ots, H. and Ginstrup, O., Acta Chem. Scand. 24 (1970) 1067.
17. Sunner, S. and Wadsö, I., Science Tools 13 (1966) 1.
18. Fronaeus, S. in Jonassen, H.B. and Weissberger, A., Technique of Inorg. Chem., Interscience, N.Y., London 1963, Vol. 1, Chapter 1.
19. Ahrland, S., Chatt, J., Davies, N.R. and Williams, A.A., J. Chem. Soc. (1958) 264.

20. Ahrland, S. and Björk, N.O., Acta Chem. Scand. A 30 (1976) 249.

21. Karlsson, R. and Kullberg, L., Chem. Scr. 9 (1976) 54.

22. Arnek, R., Arkiv Kemi 32 (1970) 81.

23. Christensen, J.J., Ruckman, J., Eatough, D.J. and Izatt, R.M., Thermochim. Acta 3 (1972) 203.

24. Berne, E. and Leden, I., Sv. Kem. Tidskr. 65 (1953) 88.

25. Berne, E. and Leden, I., Z. Naturforsch. 8a (1953) 719.

26. Leden, I. and Parch, C., Acta Chem. Scand. 10 (1956) 535.

27. Leden, I., Acta Chem. Scand. 10 (1956) 540, 812.

28. Leden, I. and Nilsson, R., Z. Naturforsch. 10a (1955) 67.

29. Ahrland, S., Helv. Chim. Acta 50 (1967) 306.

30. Ahrland, S. in J.J. Lagowski, Ed., The Chemistry of Non-Aqueous Solvents, Academic Press, New York 1977, Vol. 5.

31. Criss, C.M. and Salmon, M. in Covington, A.K. and Dickinson, T., Physical Chemistry of Organic Solvent Systems. Plenum Press, London and New York 1973, p. 253.

32. Eisenberg, D. and Kauzmann, W., The Structure and Properties of Water. Clarendon Press, Oxford 1969.

33. Franks, F., Water a Comprehensive Treatise, vol. 1, The Physics and Physical Chemistry of Water. Plenum Press, N.Y., London 1972.

34. Alexander, R., Owensby, D.A., Parker, A.J. and Waghorne, W.E., Austral. J. Chem. 27 (1974) 933.

35. Ahrland, S. and Björk, N.O., Acta Chem. Scand. A 28 (1974) 823.

36. Sandström, M., Ahrland, S., Johansson G. and Persson, I., To be published.

37. Wayland, B.B. and Schramm, R.F., Chem. Comm. (1968) 1465.

38. Price, J.H., Schramm, R.F. and Wayland, B.B., Chem. Comm. (1970) 1377.

39. Gaizer, F. and Johansson, G., Acta Chem. Scand. 22 (1968) 3013.

40. Ahrland, S. and Björk, N.O., Coord. Chem. Rev. 16 (1975) 115.

41. Manahan, S.E. and Iwamoto, R.T., Inorg. Chem. 4 (1965) 1409.

42. Foll, A., Le Démézet, M. and Courtot-Coupez, J., Bull. Soc. Chim. Fr. (1972) 408.

43. Foll, A., Le Démézet, M. and Courtot-Coupez, J., Bull. Soc. Chim. Fr. (1972) 1207.

44. Izatt, R.M., Johnsson, H.D., Watt, G.D. and Christensen, J.J., Inorg. Chem. 6 (1967) 132.

45. Arnek, R., Arkiv Kemi 24 (1965) 531.

46. Kullberg, L., Thermodynamics of Metal Complex Formation in Aqueous Solution. Diss. Lund 1974. p. 27.

47. Le Démézet, M., Madec, C. and L'Her, M., Bull. Soc. Chim. Fr. (1970) 365.

48. Synnott, J.C. and Butler, J.N., J. Phys. Chem. 73 (1969) 1470.

49. Fronaeus, S., Acta Chem. Scand. 4 (1950) 72.

50. Johansson, L., Coord. Chem. Rev. 3 (1968) 293.